

ON THE WENTZEL-BRILLOUIN-KRAMERS APPROXIMATE
SOLUTION OF THE WAVE EQUATION

BY LLOYD A. YOUNG

Department of Physics, University of Michigan

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT
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ABSTRACT

A discussion of the Wentzel-Brillouin-Kramers method of obtaining an approximate solution of the wave equation is given from the point of view that it forms a link between the quantum theory of Bohr and the new quantum mechanics. This becomes clear when one compares the probability distributions (see Figs. 2 and 3) and calculates the mean values $\bar{r}^k$ (see Table I). It is shown that for high quantum numbers these become the classical values. The method leads also, as shown by Zwaan, to quantization by the classical phase integrals with the use of half-integer quantum numbers. In the last section the method is applied to the charged shell atom model. It is shown that the condition of smooth joining of the wave function is practically equivalent to half-integer quantization of the sum of the inner and outer phase integrals. Of course there is no longer a sharp distinction between penetrating and non-penetrating orbits. The Landé formula for the doublet separations is derived. The value of $\psi^2(0)$, which occurs in the calculation of the hyperfine separations in 2S states, is also given.

I. GENERAL CHARACTER OF WENTZEL-BRILLOUIN-KRAMERS APPROXIMATE SOLUTION

THE method proposed by Wentzel and Brillouin and later developed by Kramers and Zwaan¹ for obtaining an approximate solution of the one-dimensional wave equation²

$$\psi''(x) + Q^2(x)\psi = 0 \quad (1)$$

where $Q^2(x) = (8\pi^2m/h^2)(E - V(x))$ in which E is the total energy and $V(x)$ the potential energy of the system consists, as is well known, in substituting into Eq. (1) an expression of the form

$$\psi = \exp \left\{ \frac{2\pi i}{h} \left(S_0 + \frac{h}{2\pi} S_1 + \frac{h^2}{4\pi^2} S_2 + \cdots \right) \right\}$$

where $S_0, S_1, S_2, \cdots$ are functions of x to be determined. One finds easily by successively equating the coefficients of equal powers of $h/2\pi$ to zero that

$$S_0 = \pm \int^x Q dx$$

¹ G. Wentzel, *Zeits. f. Physik* **38**, 518 (1926); L. Brillouin, *C. R. Juli*, 1926; H. A. Kramers, *Zeits. f. Physik* **39**, 828 (1926); H. A. Kramers and G. P. Ittmann, *Zeits. f. Physik* **58**, 217 (1929); A. Zwaan, *Utrecht Dissertation*, 1929.

² It should be noticed that $Q(x)$ is proportional to the linear momentum $p(x)$ and therefore to the velocity $v(x)$.

$$\begin{array}{ccc}
 S_1 & = & + \frac{i}{2} \log Q \\
 \vdots & & \vdots \\
 \vdots & & \vdots
 \end{array}$$

One obtains therefore as a first approximation to a solution of Eq. (1)

$$\psi_{\text{appr}} = Q^{-1/2} \left\{ c_1 \exp \left(\frac{2\pi i}{h} \int^x Q dx \right) + c_2 \exp \left(- \frac{2\pi i}{h} \int^x Q dx \right) \right\}$$

The integration constants c_1 and c_2 must now be so chosen that in regions where a motion was possible classically ($Q^2(x) > 0$) ψ has an oscillatory character while in regions where $Q^2(x) < 0$ we have solutions behaving as a linear combination of increasing and decreasing exponentials.

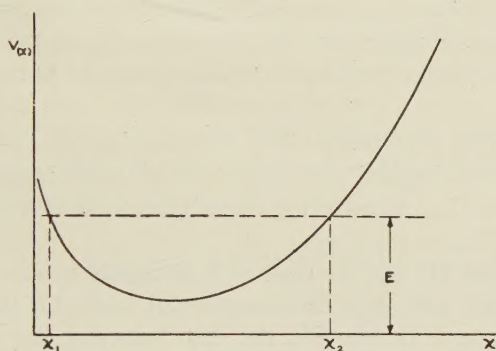


Fig. 1.

If, for example, we are considering a potential function of the type sketched in Fig. 1 the approximate solution will have the forms

$$\begin{aligned}
 \psi_{\text{appr}} &= A Q^{-1/2} \cos \left\{ \int_{x_1}^x Q dx + \delta \right\} & x_1 < x < x_2 \\
 &= B Q^{-1/2} \exp \left\{ \int_x^x Q dx \right\} & x < x_1 \\
 &= C Q^{-1/2} \exp \left\{ \int_{x_2}^x Q dx \right\} & x > x_2.
 \end{aligned} \tag{2}$$

These solutions have been so chosen that they become zero for $x = \pm \infty$ as they must if they are to correspond to an eigenfunction of the discrete spectrum of the wave equation.

When the expressions (2) are approximations to one and the same exact solution it is clear that there must be relations connecting the constants of amplitude and phase A , B , C , and δ . These relations are given by Kramers and Zwaan. They say that an increasing exponential solution like $\psi_{\text{appr}} = Q^{-1/2} \exp \left\{ \int^x Q dx \right\}$ is "connected" with an oscillatory solution $\psi_{\text{appr}} = Q^{-1/2} \cos \left\{ \int^x Q dx + \delta \right\}$.

$\cos \left\{ \int^x Q dx - \pi/4 \right\}$ while a decreasing exponential solution $\frac{1}{2}Q^{-1/2} \exp \left\{ - \int^x Q dx \right\}$ must connect with an oscillatory function $Q^{-1/2} \cos \left\{ \int^x Q dx + \pi/4 \right\}$. These formulas completely determine δ but the constants A , B , and C are determined only within a common multiplicative constant which may be fixed by normalization.

The value of this approximate solution is two-fold; first, of course, it can lead to valuable results in cases where the exact solution is unknown or difficult to handle; in the second place it has the advantage that it is a link between the classical quantum theory of Bohr and the exact quantum mechanics. One may say that it shows how from the viewpoint of the latter, at least in the case of one-dimensional problems, the classical physicist ought to have treated his problems to obtain the best results. We will illustrate this in general:

a. by showing that the approximate solution leads to a determination of the energies by quantization of the classical action integrals with the sole difference that half-integer quantum numbers must be used instead of whole numbers.

b. by considering the probability distribution $P_{\text{appr}} = \text{const} \psi^2_{\text{appr}}$ and comparing it with the classical probability which is inversely proportional to the velocity, that is $P_{\text{class}} = \text{const}/v = \text{const}/Q$ as well as with the exact probability functions $P_{\text{exact}} = \text{const} \psi \bar{\psi}$.

In sections II and III for the case of hydrogenic atoms and the charged shell atom model we will show in more detail how the Wentzel-Brillouin-Kramers approximate solution fills the gap between the older and newer theories.

2. If we consider a potential function of the type sketched (Fig. 1) corresponding to an allowed energy E such that the classical motion was periodic and bounded by the points x_1 and x_2 we may apply the connection formulas at these points obtaining as our approximate solution for this region either

$$Q^{-1/2} \cos \left\{ \int_x^x Q dx - \pi/4 \right\}$$

or

$$Q^{-1/2} \cos \left\{ \int_x^{x_2} Q dx - \pi/4 \right\}$$

We shall require that these two expressions join smoothly at every point x of the interval x_1 to x_2 (or, in other words the two must be identical). Since the solutions are determined only within an arbitrary multiplicative constant we must have $\psi_1'/\psi_1 = \psi_2'/\psi_2$ where ψ_1 and ψ_2 denote the two alternative cosine-like solutions for this region. This condition requires that

$$\tan \left\{ \int_{x_1}^x Q dx - \pi/4 \right\} = - \tan \left\{ \int_x^{x_2} Q dx - \pi/4 \right\} \quad (3)$$

This has the solution $\int_{x_1}^x Q dx = -\int_x^{x_2} Q dx + (n_x + \frac{1}{2})\pi$ from which we see

$$\int_{x_1}^{x_2} Q dx = (n_x + \frac{1}{2})\pi. \quad (4)$$

This relation determines the allowed energies and from our previous remark concerning the relationship between $Q(x)$ and the linear momentum $p(x)$ we see that this is equivalent to quantization by the action integrals of the Bohr theory with the single difference that half-integers now appear instead of the integers of the older theory.

$$I = \oint p dq = (n + \frac{1}{2})h \text{ instead of } I = nh.$$

This was first made clear by Kramers and later expressed in practically the above form by Zwaan in his Utrecht dissertation. It is felt that this affords a justification for the half-integer quantization which was found empirically to be so successful in certain problems, particularly in the interpretation of the vibrational spectra of diatomic molecules.

3. In discussing the character of the approximate solution we shall speak of the derived probability functions rather than the solutions themselves. As unnormalized probability functions we have

$$\begin{aligned} P &= \frac{1}{4}Q^{-1} \exp \left\{ -2 \int_{x_1}^x Q dx \right\} & x < x_1 \\ &= Q^{-1} \cos^2 \left\{ \int_{x_1}^x Q dx - \pi/4 \right\} & x_1 < x < x_2 \\ &= \frac{1}{4}Q^{-1} \exp \left\{ -2 \int_x^{x_2} Q dx \right\} & x > x_2. \end{aligned} \quad (5)$$

First of all we notice that in the region $x_1 < x < x_2$ the probability is a positive oscillatory function with an amplitude equal to Q^{-1} —exactly the classical probability function. The close relation of this probability to the corresponding classical quantity is brought out if we write

$$P = Q^{-1} \cos^2 \left\{ \int_{x_1}^x Q dx - \pi/4 \right\}$$

in the equivalent form

$$P = \frac{1}{2}Q^{-1} - \frac{1}{2}Q^{-1} \sin \left\{ 2 \int_{x_1}^x Q dx \right\}. \quad (6)$$

The first term in this expression is just the classical probability. In calculating mean values the second term will contribute little due to its alternating sign and we will obtain to a first approximation the classical result with half-integer quantum numbers.³ In the limit of large quantum numbers the ratio of the contribution of the second term to that of the first will vanish.

³ It is now clear that the classical analogue of the matrix element X_{nm} connected with the transition between two states characterized by, say, the energies E_n and E_m is given by

The probability functions in the tail regions ($x < x_1$, $x > x_2$) had no meaning in the Bohr theory and it may be shown that their contribution may be considered as a small correction to the results obtained from the region in which a motion was classically possible. In the exact wave mechanical theory, however, the tail regions are not so sharply marked off from the interval⁴ x_1 to x_2 and it may be shown that the results obtained by using the approximate solution lie between those of the classical theory and those of the Schrödinger theory.

Summarizing we see that the approximate probability function $P_{\text{appr}} = c\psi_{\text{appr}}^2$ has in common with the exact probability $P_{\text{exact}} = c\psi_{\text{exact}}^2$ an oscillatory character in the region $x_1 < x < x_2$ and the existence of exponentially decreasing tails. With the classical probability function it has in common that at x_1 and x_2 it becomes infinite⁵ and that the amplitude of the oscillatory part is equal to the classical probability function. See Figs. 2 and 3.

II. APPLICATION TO HYDROGENIC ATOMS

4. The three dimensional motion of a charged particle (electron) in a central Coulomb field is described by a wave equation of the form

$$\Delta_3\psi + \frac{8\pi^2m}{h^2}\left(E - \frac{Ze}{r}\right)\psi = 0$$

where Δ_3 is the Laplace operator for three dimensions. Introduction of spherical polar coordinates allows the separation of this partial differential equation and the solution may be written $\psi = R(r)y_l(\theta, \phi)$ and y_l is a spherical harmonic of the l^{th} order. By the substitution $w = rR$ the radial equation is reduced to the form

$$w'' + Q^2(r)w = 0$$

where

$$Q^2(r) = \frac{2Z}{r} - \epsilon - \frac{l(l+1)}{r^2}.$$

In this expression Z/r is the potential energy of an electron at a distance r from a Z -fold charged positive nucleus, ϵ is the total energy of the electron, and l has the physical meaning of total angular momentum.⁶

$$X_{nm} = \int \frac{X}{(Q_n Q_m)^{1/2}} dx \sqrt{\left[\int \frac{dx}{Q_n} \int \frac{dx}{Q_m} \right]^{1/2}}.$$

⁴ From Eq. (1) we see that at the points x_1 and x_2 $\psi''(x) = 0$ so that these points are the outer inflection points of the exact solution.

⁵ ψ_{appr}^2 is, however, still integrable.

⁶ All quantities are measured in the rational units first proposed by Hartree (D. R. Hartree, Proc. Camb. Phil. Soc. **24**, 89, 1928). In this system of units energy is measured in multiples of the negative energy of the hydrogen atom in its lowest stationary state; distances in terms of a unit equal to the radius of the first Bohr orbit of hydrogen; and time in units $1/4\pi cR$ where c is the velocity of propagation of light in vacuum and R is the Rydberg constant in sec^{-1} .

The above equation is of the form considered in the preceding section and the approximate solution considered there will be applied to the determination of the properties of hydrogenic atoms. Naturally, we ask first as to whether or not the correct energies are obtained when half-integer quantization is employed. We must evaluate the integral

$$\int_{r_1}^{r_2} \left[\frac{2Z}{r} - \epsilon - \frac{l(l+1)}{r^2} \right]^{\frac{1}{2}} dr$$

and equate it to $(n_r + \frac{1}{2})\pi$. The above integral was well known in the older theory giving

$$\pi(Z/\epsilon^{1/2} - [l(l+1)]^{1/2}) = (n_r + 1/2)\pi$$

or

$$\epsilon = \frac{Z^2}{(n_r + \frac{1}{2} + [l(l+1)]^{1/2})^2}$$

It is apparent that we do not obtain the familiar Balmer formula except in the limit of large l values. If, however we replace $l(l+1)$ by $(l + \frac{1}{2})^2$ the correct result is obtained.

We shall now investigate the properties of the approximate eigenfunctions more closely. In the region $r < r_1$ we may choose either the positive or the negative exponential. This corresponds to our freedom of choice of either of the two roots of the indicial equation of the exact solution. We consider only the root which gives a solution vanishing at the origin and which behaves for very small values of r like r^{l+1} . The approximate solution based upon the negative exponential behaves for r very small like $r^{[l(l+1)]^{1/2} + \frac{1}{2}}$. Again the replacement of $l(l+1)$ by $(l + \frac{1}{2})^2$ leads to an agreement between the approximate and exact solutions. This is considered to be a sufficient argument for the consistent use of half-integers not only for the radial quantum number but for the azimuthal quantum number as well. Hereafter we shall consider $Q^2(r) = 2Z/r - \epsilon - (l + \frac{1}{2})^2/r^2$ instead of the expression previously used.

5. From the wave mechanics it has become clear that most if not all observable properties of an atomic system can be expressed in terms of mean values of certain functions of the coordinates of the system. In the case of hydrogenic atoms for example the mean values $\overline{r^k}$ where k is a positive or negative integer, are very important. If P represents the probability function as a function of r we may write

$$\overline{r^k} = \frac{\int r^k P dr}{\int P dr}$$

This expression may be used for the calculation of mean values classically if $P = P_{\text{class}}$ and the range of integration is over that region of the variable

where $Q^2(r) > 0$; wave mechanically if $P = P_{\text{exact}}$ and the range of integration is extended from 0 to ∞ ; and by the Wentzel-Brillouin-Kramers approximation method if the approximate probability functions (5) are used and the integration taken over the entire range of the variable. For the latter case we may write

$$\overline{r^k} = \frac{\int_0^{r_1} P_{\text{app}}^{(1)} r^k dr + \int_{r_1}^{r_2} P_{\text{app}}^{(2)} r^k dr + \int_{r_2}^{\infty} P_{\text{app}}^{(3)} r^k dr}{\int_0^{r_1} P_{\text{app}}^{(1)} dr + \int_{r_1}^{r_2} P_{\text{app}}^{(2)} dr + \int_{r_2}^{\infty} P_{\text{app}}^{(3)} dr} = \frac{I_k^{(1)} + I_k^{(2)} + I_k^{(3)}}{I_0^{(1)} + I_0^{(2)} + I_0^{(3)}}.$$

By referring to Eqs. (6) we see that

$$I_k^{(2)} = \int_{r_1}^{r_2} P_{\text{app}}^{(2)} r^k dr = \int_{r_1}^{r_2} \left(\frac{1}{2} P_{\text{class}} - \frac{1}{2} Q^{-1} \sin \left\{ 2 \int_r^r Q dr \right\} \right) r^k dr = C_k - U_k$$

If we now consider

$$(\overline{r^k})_{\text{class}} = C_k / C_0$$

we obtain

$$\overline{r^k} \cong \overline{r^k}_{\text{class}} \left(1 + \frac{I_k^{(1)} - U_k + I_k^{(3)}}{C_k} - \frac{I_0^{(1)} - U_0 + I_0^{(3)}}{C_0} \right). \quad (7)$$

The above integrals were evaluated after making certain simplifying assumptions. It can be shown that for high total quantum numbers the correction terms vanish. In general, using (7) we get results lying between the classical values with half integer quantum numbers and the exact values. As an example we have tabulated $\overline{r^2}$.

TABLE I. *Hydrogenic atoms.*

	Class	Class (half-integers)	W.B.K.	Exact
$n=1, l=0$	1.0	2.1	2.5	3.0
$n=2, l=0$	34.0	38.5	40.8	42.0
$n=2, l=1$	16.0	26.5	28.6	30.0

In Figs. 2 and 3 the radial probability functions for the 3s and 3d states of hydrogen respectively have been plotted as a function of r . These examples illustrate the relation of the Wentzel-Brillouin-Kramers approximation to the results obtained by the exact wave mechanics.

6. In treating the frequency splitting in hyperfine structure due to the interaction of the extra-nuclear electrons with the nuclear magnetic moment it becomes necessary to calculate the magnetic field at the nucleus due to the orbital motion of the electron. This may be shown, in a classical way, to be proportional to $\overline{r^{-3}}$ and it would seem probable that the wave mechanical treatment should follow the classical treatment closely. However from the

fact that the exact solution of the Schrödinger equation behaves in the neighborhood of the origin like r^{l+1} and the probability distribution like $r^{2(l+1)}$ it is clear that $\overline{r^{-3}}$ diverges for s -states ($l=0$). This difficulty is only cleared

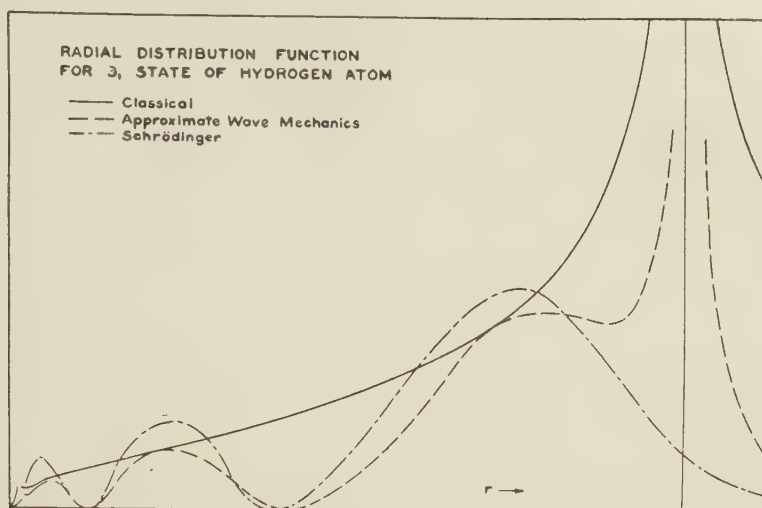


Fig. 2.

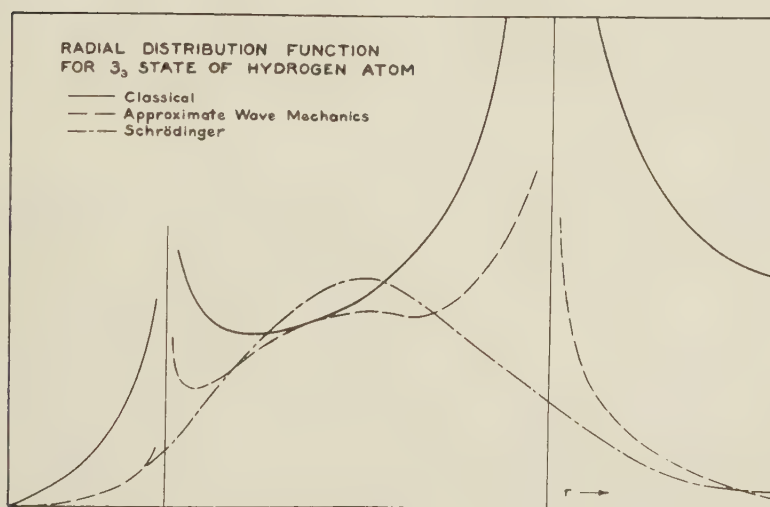


Fig. 3.

up when we treat the problem by means of the Dirac theory of the spin electron. Fermi and Hartree⁷ have shown that for s -states we have only to replace $l \times \overline{r^{-3}}$ by $\frac{1}{2} R^2(0)$ where $R(0)$ is the value of the normalized radial eigenfunction at the origin, to obtain the correct results. Thus for $l \neq 0$ we have $\overline{r^{-3}}$:

⁷ E. Fermi, *Zeits. f. Physik* **60**, 320 (1930); D. R. Hartree, *Proc. Camb. Phil. Soc.* **25**, 225 (1929).

Classical	Classical (half integers)	W. B. K.	Exact
$\frac{Z^3}{n^3(l+1)^3}$	$\frac{Z^3}{n^3(l+\frac{1}{2})^3}$	$\frac{Z^3}{n^3(l+\frac{1}{2})^3}(1 + \text{corr.})$	$\frac{Z^3}{n^3l(l+\frac{1}{2})(l+1)}$

While for $l=0$ we have:

$\frac{1}{2}R^2(0)$		$\frac{1}{2}R^2(0)$	
Classical	Classical (half integers)	W. B. K.	Exact
$\frac{Z^3}{n^3}$	$\frac{4Z^3}{n^3}$	const. $\frac{Z^3}{n^3}(1 + \text{corr.})$	$\frac{2Z^3}{n^3}$

For the case of $\frac{1}{2}R^2(0)$ by the Wentzel-Brillouin-Kramers approximation we are particularly interested to find out whether or not we obtain good agreement with the exact value since analogous methods when applied to the observed hyperfine structure of the alkali atoms can give valuable information concerning the structure of these nuclei.

For this case we may write

$$\frac{1}{2}R^2(0) = \frac{1}{2} \frac{\lim_{r=0} \frac{1}{4r^2Q} \exp \left\{ -2 \int_{r_1}^r Q dr \right\}}{I_0^{(1)} + C_0 - U_0 + I_0^{(3)}}.$$

Calculation of the numerator and using the values of the normalization integrals given in the appendix we find

$$\frac{1}{2}R^2(0) \cong \frac{\exp 2}{\pi} \frac{Z^3}{n^3} \left(1 - \frac{1}{24n^2} \right) \left(1 - \frac{I_0^{(1)} - U_0 + I_0^{(3)}}{C_0} \right). \quad (8)$$

A numerical calculation for the states having $n=1, 2, \infty$ was made and the coefficients of Z^3/n^3 were found to be 2.60, 2.40, and 2.35. These are to be compared with the exact coefficient which is just 2.

III. APPLICATION TO THE CHARGED SHELL ATOM MODEL

7. The difficulties encountered in representing the properties of an alkali atom in the quantum mechanics are much the same as in the older theories. The calculation of the interaction between all the electrons of the atom seems to be a problem of the future. At present the only possibility seems to be to represent by some simple model as many of the properties of the atom as possible. The simplest mode of procedure is to assume that the core electrons act as a spherically symmetrical charge distribution about the nucleus and that the optical electron moves in the field of the nucleus and this charge distribution. Some progress has been made in the determination of the appropriate charge distribution by various investigators. The unfortunate thing about their results, however, is that the mathematical methods to which they lead are of a purely numerical or graphical type. Clearly one must idealize the problem if one is to obtain results of any generality. The simplest idealization that one can make is to consider the core electrons con-

centrated in one or more spherical surface distributions of charge about the nucleus. If we adopt this charged shell model our mode of procedure is quite clear.

Consider an atom with a Z -fold charged nucleus surrounded by a spherically charged shell at a distance r_0 from the nucleus. Suppose the total charge in this shell to be $Z - z$ electrons. We will then have to deal with two functions Q^2 instead of one; namely

$$Q_i^2(r) = \frac{2Z}{r} - \frac{2(Z - z)}{r_0} - \epsilon - \frac{(l + \frac{1}{2})^2}{r^2}$$

$$Q_0^2(r) = \frac{2Z}{r} - \epsilon - \frac{(l + \frac{1}{2})^2}{r^2}.$$

We shall seek solutions of the two differential equations

$$w_i'' + Q_i^2(r)w_i = 0 \quad r < r_0$$

$$w_0'' + Q_0^2(r)w_0 = 0 \quad r > r_0$$

which join smoothly at $r = r_0$ (a smooth join means $w_i'/w_i = w_0'/w_0$ at $r = r_0$). Freedom of choice of r_0 still remains and we shall suppose that it has been chosen to lie within the region where a motion was possible classically.

The first question we must consider is concerning half-integer quantization. To answer this consider the two approximate solutions

$$w_i = Q_i^{-1/2} \cos \left\{ \int_{r_1}^r Q_i dr - \pi/4 \right\}$$

$$w_0 = Q_0^{-1/2} \cos \left\{ \int_r^{r_2} Q_0 dr - \pi/4 \right\}$$

The smooth joining condition given above leads to

$$- \tan \left\{ \int_{r_1}^{r_0} Q_i dr - \pi/4 \right\} - \frac{1}{2} Q_i^{-2}(r_0) Q_i'(r_0)$$

$$= \tan \left\{ \int_{r_1}^{r_2} Q_0 dr - \pi/4 \right\} - \frac{1}{2} Q_0^{-2}(r_0) Q_0'(r_0)$$

(note that $Q_i(r_0) = Q_0(r_0)$) which by the introduction of the notation

$$\int_{r_1}^{r_0} Q_i dr - \pi/4 = \alpha$$

$$\int_{r_0}^{r_2} Q_0 dr - \pi/4 = \beta$$

$$\frac{1}{2} Q_0^{-2}(r_0) \{ Q_0'(r_0) - Q_i'(r_0) \} = \eta$$

may be written

$$\tan \alpha + \tan \beta = \eta.$$

If $Q_0'(r_0) - Q_i'(r_0)$ were equal to zero (the inequality existing corresponds to the fact that the electric force has a discontinuity at r_0) we would have $\eta = 0$ whence

$$\tan \alpha + \tan \beta = 0$$

$$\alpha + \beta = \eta_r \pi$$

or

$$\int_{r_1}^{r_0} Q_i dr + \int_{r_0}^{r_2'} Q_0 dr = (\eta_r + \frac{1}{2})\pi.$$

That is to the order of accuracy with which we may replace η by zero half-integer quantization is retained. The method used here should be compared with the corresponding procedure used in the treatment of hydrogenic atoms.

When η may not be considered zero it is necessary to consider

$$\tan \alpha + \tan \beta = \eta.$$

In case η is small we may write

$$\int_{r_1}^{r_0} Q_i dr + \int_{r_0}^{r_2} Q_0 dr = (\eta_r + \frac{1}{2})\pi + \tan^{-1} \eta.$$

The evaluation of this expression gives the possible energies for the charged shell model as a function of the quantum numbers and of r_0 —that is a Rydberg formula which is the analogue of the Balmer formula for the terms of hydrogen-like atoms.

It is perhaps worth while to remark that the deviation from half-integer quantization found here is a defect of the charged shell model and that if we replaced it by a model using the charge distributions of Hartree or Fermi⁸ we would again have half-integer quantization.

8. We can now use the approximate wave functions to calculate the quantities $\overline{r^k}$ for alkali-like atoms. All correction integrals will be neglected (in other words, the calculation is purely classical) since the value of r_0 is so uncertain, that greater accuracy is unwarranted. We have, then, to consider the integrals

$$\int_{r_1}^{r_0} r^k Q_i^{-1} dr \quad \text{and} \quad \int_{r_0}^{r_2} r^k Q_0^{-1} dr$$

These may be replaced approximately by

$$\int_{r_1}^{r_1'} r^k Q_i^{-1} dr \quad \text{and} \quad \int_{r_2'}^{r_2} r^k Q_0^{-1} dr$$

where r_2' and r_1' are the inner and outer roots of Q_0^2 and Q_i^2 respectively.

⁸ D. R. Hartree, Proc. Camb. Phil. Soc. **24**, 89 (1928); E. Fermi, Zeits. f. Phys. **48**, 73 (1928)

Using the notation introduced in section II. for hydrogenic atoms we may write immediately:

$$\overline{r^k} = \frac{E^{-1/2}C_k^{(i)} + \epsilon^{-1/2}C_k^0}{E^{-1/2}C_0^{(i)} + \epsilon^{-1/2}C_0^{(0)}} \quad (9)$$

where we have put

$$E = \epsilon + \frac{2(Z - z)}{r_0}.$$

Application of this formula for $\overline{r^{-3}}$ gives

$$\overline{r^{-3}} = \frac{Zz^2}{n_{\text{eff}}^3(l + \frac{1}{2})^3} \quad (10)$$

where $\epsilon = Z^2/n_{\text{eff}}^2$ and we neglect $\epsilon^{-1}C_3^{(0)}$ against $E^{-1}C_3^{(i)}$ and $E^{-1}C_0^{(i)}$ against $\epsilon^{-1}C_0^{(0)}$. This gives the well-known Landé formula⁹ for the doublet separations in optical spectra.

Following Schrödinger¹⁰ we could choose r_0 as the perihelion distance of the parabolic orbits of hydrogenic atoms $r_0 = (l + \frac{1}{2})^2/2z$. It is felt, however that this choice of r_0 has lost some of its physical meaning since the development of wave mechanics.

A procedure analogous to that used for hydrogenic atoms for the determination of $\frac{1}{2}R^2(0)$ gives

$$\frac{1}{2}R^2(0) \cong 2.35 \cdot \frac{Zz^2}{n_{\text{eff}}^3} \left(1 - \frac{2z}{3Z} + \dots \right).$$

Replacement of " $2Z^3/n^3$ " by the above expression in the formula for the frequency separation in hyperfine structure of the 2S states of alkali atoms¹¹ gives for the product of the Landé g -value of the nucleus and the mechanical moment of nucleus and electron

$$\begin{aligned} g(i)(i + \frac{1}{2}) &= 2.51 \text{ for Na} \\ &= 1.76 \text{ for Rb} \\ &= 3.67 \text{ for Cs} \\ &= 5.33 \text{ for Tl.} \end{aligned}$$

Fermi, using his statistical atom model and numerical calculation of the eigenfunctions, has given the values 4.11 and 1.89 for Na and Cs respectively.

⁹ The analogous approximation can always be made when k is negative. For example, we obtain

$$\overline{r^{-4}} = \frac{\frac{3}{2}Z^2 - \frac{1}{2}(l + \frac{1}{2})^2E}{(l + \frac{1}{2})^5z\epsilon^{-3/2}} \cong \frac{3}{2} \frac{Z^2z^2}{n_{\text{eff}}^3(l + \frac{1}{2})^5}$$

Of course this like (10) will hold only for $l > 0$ since for $l = 0$, $\overline{r^{-3}}$ and $\overline{r^{-4}}$ diverge. For positive values of k similar approximations may be made giving, for example

$$\overline{r^2} = \frac{1}{2} \frac{n_{\text{eff}}^2}{z^2} \left\{ 5n_{\text{eff}}^2 - 3 \left(l + \frac{1}{2} \right)^2 \right\}.$$

¹⁰ E. Schrodinger, Zeits. f. Physik **4**, 347 (1921).

¹¹ S. Goudsmit and L. A. Young, Nature **125**, 461 (1930).

It is unfortunate that it is difficult to give a criterion for the accuracy of these results. One can hardly expect them to be correct except as to order of magnitude.

APPENDIX

MEAN VALUE INTEGRALS

In calculating the mean values $\overline{r^k}$ for hydrogenic atoms the following integrals were encountered:

$$I_k^{(1)} = \frac{1}{4} \int_0^{r_1} r^k Q^{-1} \exp \left\{ -2 \int_r^{r_1} Q dr \right\} dr$$

$$C_k = \frac{1}{2} \int_{r_1}^{r_2} r^k Q^{-1} dr$$

$$U_k = \frac{1}{2} \int_r^{r_2} r^k Q^{-1} \sin \left\{ 2 \int_{r_1}^r Q dr \right\} dr$$

$$I_k^{(3)} = \frac{1}{4} \int_{r_2}^{\infty} r^k Q^{-1} \exp \left\{ -2 \int_{r_2}^r Q dr \right\} dr.$$

The integral C_k was evaluated exactly, but it was necessary to introduce simplifying assumptions in evaluating the correction integrals $I_k^{(1)}$, U_k , and $I_k^{(3)}$. It was found that

$$\begin{aligned} C_k &= \frac{1}{2} \pi \epsilon^{-1/2} P^{(k+1)/2} P_{-(k+2)} \left(\frac{1}{2} S P^{-1/2} \right) & k < -1 \\ &= \frac{1}{2} \pi \epsilon^{-1/2} P^{(k+1)/2} P_{k+1} \left(\frac{1}{2} S P^{-1/2} \right) & k \geq -1 \end{aligned}$$

where P is the product of the roots of Q^2 , r_1 and r_2 , and $P_m(x)$ is the m -th Legendre polynomial of the argument x . No general formula was found for the integral $U_{(k)}$ but after simplifying approximations had been made it was possible to evaluate the integrals for special values of k with the results:

$$U_2 \cong \frac{(-1)^{n_r}}{16} \pi \epsilon^{-1/2} \left[3D^2 S \frac{J_1(\xi)}{\xi} + S^3 J_0(\xi) \right]$$

$$U_{-2} \cong (-1)^{n_r} \pi \epsilon^{-1/2} S^{-1} \left[J_0(\xi) + \left(\frac{D}{S} \right)^2 \frac{J_1(\xi)}{\xi} + 3 \left(\frac{D}{S} \right)^4 \frac{J_2(\xi)}{\xi^2} + \dots \right].$$

The values of U_k for other values of k were obtained by use of the recurrence relation

$$U_{k-1} = \frac{2}{k+1} \frac{dU_k}{dS}.$$

In these relations $S = r_1 + r_2$, $D = r_2 - r_1$, $\xi = (n_r + \frac{1}{2})\pi$, and $J_n(\xi)$ is the n -th Bessel function of the argument ξ . The integrals $I_k^{(1)}$ were found to be given approximately by:

$$I_k^{(1)} \cong \frac{(l + \frac{1}{2})^{2k+2} \exp \left\{ l + \frac{1}{2} \right\}}{2^{k+1} (2l + k + 5)}.$$

Finally, for the integrals $I_k^{(3)}$ we find

$$I_2^{(3)} = \frac{1}{8} r_2^3 \epsilon^{-1/2} \exp\left(\frac{\beta}{2}\right) \left[\left(1 + \frac{1}{2\beta}\right) K_0\left(\frac{\beta}{2}\right) + \left(1 + \frac{3}{2\beta} + \frac{2}{\beta^2}\right) K_1\left(\frac{\beta}{2}\right) \right]$$

$$I_1^{(3)} = \frac{1}{8} r_2^2 \epsilon^{-1/2} \exp\left(\frac{\beta}{2}\right) \left[K_0\left(\frac{\beta}{2}\right) + \frac{\beta+1}{\beta} K_1\left(\frac{\beta}{2}\right) \right]$$

$$I_0^{(3)} = \frac{1}{8} r_2 \epsilon^{-1/2} \exp\left(\frac{\beta}{2}\right) \left[K_0\left(\frac{\beta}{2}\right) + K_1\left(\frac{\beta}{2}\right) \right]$$

$$I_{-1}^{(3)} = \frac{1}{4} \epsilon^{-1/2} \exp\left(\frac{\beta}{2}\right) K_0\left(\frac{\beta}{2}\right)$$

$$I_{-2}^{(2)} = \frac{1}{4} \beta r_2^{-1} \epsilon^{-1/2} \exp\left(\frac{\beta}{2}\right) \left[K_1\left(\frac{\beta}{2}\right) - K_0\left(\frac{\beta}{2}\right) \right]$$

$$I_{-3}^{(3)} = \frac{1}{6} \beta r_2^{-2} \epsilon^{-1/2} \exp\left(\frac{\beta}{2}\right) \left[\beta K_0\left(\frac{\beta}{2}\right) - (\beta-1) K_1\left(\frac{\beta}{2}\right) \right]$$

where $\beta = 2\epsilon^{-1/2} r_2$ and $K_\nu(x)$ is the Bessel function of the third kind of order ν .

